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PREVENTION OF STREAM POLLUTION BY DYE AND INTERMEDIATE WASTES.

By E. J. CASSELMAN, Assistant Chemist, United States Public Health Service.

Liquid wastes from the manufacture of dyes and intermediates are particularly objectionable when discharged into rivers, because of their properties of high color, bad taste, or strong odor, even in very low concentrations. When the water is to be used for drinking, these qualities are eradicated only by a comparatively great dilution; that is, the river must be large compared to the discharge from the chemical factory.

The investigation which is the basis of the report and recommendations here made was undertaken for the purpose of studying the methods of disposing of dye and intermediate wastes. Most of the work was performed at the plant of the Chemical Co. of America, with special attention given to the pollution of the Rahway River¹ by the wastes from that plant.

The plant is located at Springfield, N. J., between two forks of the river. This river forms the only natural avenue of escape for the waste liquids. The nearest connection to a sewer is over a mile away, and the expense of building to the sewer is considered prohibitive. Other methods of disposing of the waste, except by treatment, such as trucking or shipping to tidewater, are also highly expensive. The cost of evaporation, the most obvious means of purification, depends upon the method used. If it were permissible to allow spontaneous evaporation of the waste by trickling over ricks, this method could no doubt be carried on very cheaply. But such evaporation would require a large installation for the amount of waste produced here, and, furthermore, the system would not be dependable during damp, quiet weather nor in the winter. A multiple-effect method of evaporation with recovery and discharge of distillate is hardly permissible, as the odorous constituents of the wastes are usually volatile enough to distill over with the water. It is assumed, then, that a method of evaporation would be devised

¹ For the legal aspect of the case see Public Health Reports, Oct. 17, 1919, p. 2303.

for burning coal to evaporate the waste in a single effect or stage. The cost of this would be about \$0.0006 per pound of water, assuming coal costs at \$7 per net ton and that 1 pound of coal evaporates 6.5 pounds of water.

Any chemical method of waste disposal, then, must be cheaper than \$0.0006 per pound of water in order to compete with the evaporation process.

In this investigation it was hoped that treatments could be found for producing liquors that were not objectionable of themselves, so that they could be discharged into any river, regardless of its quantity of flow. The wastes that could not be treated to give such an effluent were studied with regard to pollution of the Rahway River at the plant.

Stream gaugings made at this point after an exceptionally dry period indicated that the minimum flow is about 5,000,000 gallons per day.

This work was carried out under the supervision of Prof. Earle B. Phelps, formerly of the Hygienic Laboratory, United States Public Health Service, whose suggestions were most helpful.

I. WASTES PRODUCED AND THEIR PROPERTIES.

Ortho-toluidine waste.—This waste results from the manufacture of ortho-toluidine. Ortho-toluidine is made from ortho-nitro-toluene by reduction with iron chips and sulphuric or hydrochloric acid. The product of the reaction is then steam distilled for purification after making alkaline. The distillation gives rise to two liquid wastes—a still residue and an aqueous layer in the receiver. The latter is a solution containing 0.015 per cent ¹ toluidine and is not an objectionable waste. The still residue, however, is a very disagreeable waste.

The properties of this waste are a very dark color, a highly disagreeable odor, and a composition which may conceivably consist of every high boiling intermediate reduction product of nitrotoluol. In addition, there are a slight acidity and high concentration of ferrous salt.

The quantity of this waste is, roughly, four-tenths of a gallon per pound of toluidine.

Nitrobenzene waste.—In the manufacture of nitrobenzene, benzene is nitrated with mixed sulphuric and nitric acids in a nitration kettle. The products are two liquid layers, one of which is spent acid and the other crude nitrobenzene. The spent acid is not considered a waste, as it is still strong enough to use for other purposes.

The nitrobenzene is next washed with soda ash solution to remove acidity, and two layers are again formed, the nitrobenzene and the wash solution. The nitrobenzene layer is distilled in vacuum stills

¹ Solubility in water (Seldell).

and there is no waste in connection with this procedure. The wash water is not used again and is the one waste of the process.

This wash water is naturally alkaline, from the excess of soda ash. It is a high orange yellow in color, and it smells strongly of nitrobenzene. The quantity is about one-sixth of a gallon per pound of nitrobenzene.

Monoethyl aniline wastes.—In the manufacture of monoethyl aniline from aniline and ethyl alcohol, these two substances are heated together with a catalyzer under certain conditions of temperature and pressure, and the monoethyl aniline is produced as a salt. It is then thrown out of combination with soda ash and distilled with steam, from which process two wastes are produced—a still residue and an aqueous layer in the receiver. This latter is salted in order to separate more monoethyl aniline from the water.

The still residue is of a medium brown color that of itself is not very objectionable. The odor, however, is very strong and disagreeable. In composition it is alkaline and may contain some unchanged alcohol and aniline, also monoethyl aniline and diethyl aniline, as well as side products like orthoethyl aniline, paraethyl aniline, orthoethyl monoethyl aniline, paraethyl monoethyl aniline. Inorganic sodium salts are also present. The quantity of still residue is about $1\frac{1}{2}$ gallons per pound of monoethyl aniline.

The receiver residue is little else than a suspension of monoethyl aniline in salt water. At first it is colorless, but on standing it turns to a pinkish shade. Its principal objection is its odor, which is very strong and disagreeable. In quantity it is about $2\frac{3}{4}$ gallons per pound of monoethyl aniline.

Dye wastes.—The dyes manufactured at the Chemical Co.'s plant consist of several triphenyl methane dyes and several azo-dyes. The processes generally take place in one solution, from which the final step is the removal of the solid dye by filtration or otherwise. The waste liquor comprises the residual solution.

The properties of these wastes vary considerably with the dye manufactured, but in every case they are highly colored because of failure to remove all the dye from them. In addition they frequently contain odorous compounds and concentrated salt. Their volumes are very considerable, ranging from 10 to 20 gallons per pound of dye.

Lagoon liquor.—For a year or more the wastes given above, as well as some others not studied, were stored in an artificial lagoon, and comprised some four or five million gallons at the time of this study. These wastes had, of course, had ample time for aeration and the evaporation of some of their more volatile constituents. Furthermore, it had been considerably diluted with rain water. The composition of this body of wastes varied to some extent from point to point

as a result of the difference in the wastes discharged at various times. In the main, however, it was a fairly uniform mixture except near the point of discharge from the plant, where dye wastes predominated.

The color of the main body of this liquor was a rather deep red, but there was scarcely any odor. It was 0.005 normal in acid, corresponding to about 0.25 per cent sulphuric acid; and it contained some iron, zinc, and sodium salts in small quantities. The object of treating this waste was to prevent the lagoon from becoming filled up and overflowing.

II. EXPERIMENTAL WORK.

The properties and treatment of the separate wastes were first studied, and then their treatment as mixtures in the proportions in which they were likely to be when discharged from the works, was undertaken.

In making these studies the first experiments were qualitative in nature, no regard being paid to cost of treatment. Quantitative tests were made upon the best results offered from the experiments. Most of these experiments were made in 100 or 200 cc. bottles with 100 or 200 cc. samples. Some of the quantitative tests were made with 2-liter volumes. Filtrations were made with a 10 cm. Büchner funnel and filter paper.

From data gained by the quantitative tests the wastes were treated on a scale of about 40 cubic feet (300 gallons). The apparatus consisted of the following: Two 350-gallon wooden tubs fitted with gauge glasses graduated in cubic feet, one wooden tower 3 by 3 by 4 feet, filled with coke, and another one filled with cinders; two sand filter-beds, each having an area of 1 square yard, and a depth of about 2 feet of sand and gravel; one small filter press; one small pump connected to each of the tubs and piped to discharge into any desirable piece of apparatus; two barrels arranged to empty into the tubs, for the purpose of mixing reagents. (Figs. 1 and 2.)

It is assumed that any results observed on this 300-gallon scale can be duplicated on any large scale without essential change in treatment.

Ortho-toluidine Waste.

Effect of making alkaline.—When ortho-toluidine waste was made alkaline, the iron it contained was thrown down as a sludge of ferrous hydroxide. The supernatant liquid was at first without much color, but it retained the very obnoxious odor. This liquid became very deeply colored on standing. That this was due to oxidation was shown by the fact that the reaction started at the surface, and that it could be more quickly brought about by aeration. The shade was somewhat dependent upon the alkalinity, being more bluish in strong alkali, and more greenish in weak. In acid solutions it was deep red. When nitrobenzene waste instead of lime was used for the precipi-

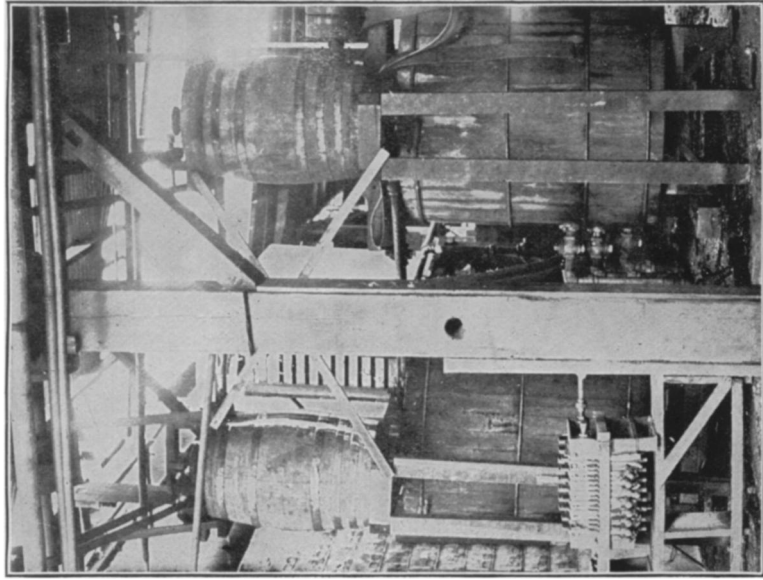


Fig. 1.—Precipitation tubs and filter press of experimental waste disposal plant, Springfield, N. J.

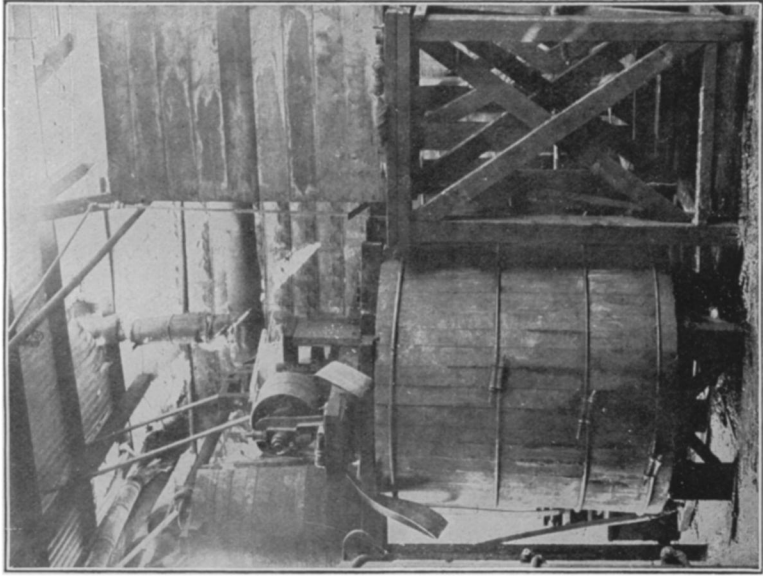


Fig. 2.—Precipitation tubs and coke tower of experimental waste disposal plant, Springfield, N. J.

tation of the iron, the deep color developed immediately, presumably from oxidation by the nitrobenzene.

The amount of lime required to neutralize and just precipitate all the iron appeared to be about 3 grams per cubic foot, but this would naturally vary with each batch of waste produced. The effect of any excess of lime over this was to make the iron sludge settle more slowly, and to decrease the blue shade of the color of the solution after oxidation.

Other precipitants.—Attempts to carry down color or odor of this alkaline solution with alum, silica, zinc hydrate, and lead sulphate were unsuccessful.

It may be concluded that precipitants are of no avail in treating toluidine waste.

Aeration.—Air was blown through alkaline filtered toluidine waste for two hours, and failed to remove much of the odor or any of the color.

Bromine.—Bromine caused a precipitation of a finely divided solid, leaving a light colored supernatant liquid (after removal of the iron).

Bleaching powder.—Bleaching powder and acid caused the precipitation of a solid tar-like substance which could be filtered off.

Quantitative experiments, made after removal of the iron by lime and after filtration, showed that the best results were obtained by the use of 10 to 30 grams per liter of chlorine, depending upon the strength of the waste. Upon filtering such a solution a light brown filtrate was obtained which turned dark on being made neutral, and still darker on being made alkaline with lime. This color could be extracted by ether in acid solution, but not in alkaline solution.

It was noted that this chlorine requirement was about the same for any particular waste no matter what the condition of its previous aeration might have been.

The color of the chlorinated solution could not be removed by precipitants like ferrous hydroxide; in fact, it became worse if nitrobenzene waste instead of slaked lime had been used for neutralizing in the first place. When enough chlorine to get the best color was used, the color removal seemed to be about 90 per cent in acid solution, 80 per cent in neutral solution, and 75 per cent in alkaline solution.

The odor of this treated waste was not much improved in intensity, but it seemed much less unpleasant.

Absorbent carbons.—Boiling alkaline, filtered toluidine waste with bone black was found to remove both odor and color. The same result was accomplished when the waste was filtered through a layer of bone black one-quarter of an inch thick. Quantitative experiments showed that roughly 1.1 cubic feet could be passed through 1 pound of the bone black before it became exhausted.

A new carbon of several grades has appeared on the market under the trade name of Superfiltchar.¹ The different grades were tried out and found to be effective against toluidine waste. In quantitative tests an amount of the carbon was weighed out into a measured volume of waste (usually 100 cc.) and allowed to stand 18 to 24 hours with occasional shaking. Table I shows the effect of various amounts of these carbons.

TABLE I.—*Effect of carbons on alkaline, filtered toluidine waste.*

Per cent.	Substance.	Residual color p. p. m. Bismarck brown dye. ¹	Residual odor.	Time.
				<i>Hours.</i>
1.44	Bone black.....	About 5.....	None.....	(²) 20
.2	Superfiltchar, oil grade.....	60.....	Faint.....	20
.3	do.....	5.....	do.....	20
.35	do.....	3.....	do.....	20
.46	do.....	2.....	Very faint.....	20
.7	do.....	None.....	None.....	16
2.0	do.....	do.....	do.....	16
.30	Filtchar.....	47.....	Perceptible.....	18
.35	do.....	40.....	Slight.....	18
.40	do.....	25.....	do.....	18
.46	do.....	24.....	Faint.....	18
.70	do.....	8.2.....	None.....	18
.80	do.....	4.6.....	do.....	18
.90	do.....	3.6.....	do.....	18
.30	do.....	80.....	Perceptible.....	1
.35	do.....	66.....	do.....	1
.40	do.....	65.....	do.....	1
.46	do.....	52.....	do.....	1
.70	do.....	7.1.....	Not observed.....	1
.80	do.....	6.4.....	do.....	1
.90	do.....	2.....	do.....	1
.40	do.....	11.....	do.....	2½
.80	do.....	4.....	do.....	2½

¹ A Bismarck brown standard solution of 100 p. p. m. was made by dissolving 100 mg. of Bismarck brown in 1 liter of distilled water, and filtering.

² By filtration.

If it be assumed that a practically odorless liquid is wanted with a color of not more than five parts per million on the arbitrary scale selected, it is seen that this can be obtained by the use of 0.3 per cent Superfiltchar, or 0.8 per cent Filtchar with a treatment of 18 hours or so. The indication of the last part of the table is that no further improvement was obtained, however, by using a time of 18 hours instead of 2½ hours in the case of Filtchar. One-quarter of an hour was too short a time.

Other absorbents.—Coke and cinders failed to remove any odor or color on a large scale in the treating plant. In the laboratory, clay from the river bank failed to remove any odor or color.

Large scale experiments.—Experiment 1: Used 35.5 cubic feet of toluidine waste and aerated it for one hour; then added enough lime (about 8 pounds) to make neutral and precipitate all the iron. This precipitate settled over night to less than 20 per cent of the total volume.

¹ From Industrial Chemical Co., 200 Fifth Avenue, New York City.

Part of the supernatant liquid was pumped through the coke filter and then through the sand filter. The coke effluent was very deeply colored as was also the sand effluent. There was some slight improvement in odor.

Another part of the supernatant liquid was pumped through the cinder filter and then through the sand filter. The effluents from both cinders and sand were highly colored and unsatisfactory, although there was some improvement in odor.

Experiment 2: To 44.2 cubic feet of toluidine waste, after aeration, 8 pounds of lime were added as milk of lime. Pumped part of the supernatant liquid through the cinders first and sand filter afterwards.

To 4.75 cubic feet of this effluent was added 34 pounds of bleaching powder (10 per cent chlorine) and 1,220 cc. of 94 per cent sulphuric acid. This should have released 54 ounces of chlorine for chlorination, corresponding to 11.5 ounces per cubic foot of solution, or 11.5 grams per liter of solution.

After standing several hours, a thick foam was observed. The liquid beneath was medium brown in color, and neutral; it had a rather penetrating odor of chlorine. No improvement was obtained by filtering this liquid through cinders and sand.

This result checked the best results that could be expected from the laboratory experiments, but the effluent could hardly be considered satisfactory to discharge into the Rahway River.

Nitrobenzene Waste.

Precipitants.—The following precipitants failed to remove odor or color: $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Si}(\text{OH})_4$, $\text{Ca}(\text{OH})_2$, CaSO_4 , $\text{Zn}(\text{OH})_2$, and PbSO_4 .

Absorbents.—Clay from the river bank, blast-furnace slag, open-hearth slag, coke, charcoal, cinders, and bone black failed to remove odor or color.

Acid.—Acid caused a precipitation which was very finely divided. The supernatant liquid retained a yellow color and the original odor. The precipitate went into solution on warming, and fell out again on recooling.

Solvents.—Benzene and ether both failed to remove color from the nitrobenzene waste.

Bleaching powder.—Bleaching powder in acid solution gave a precipitate, which removed most of the color and odor.

Large scale experiments were not performed because of the discontinuance of the manufacture of nitrobenzene.

Monoethyl Aniline Waste. Receiver Liquor.

Bromine.—Bromine precipitated a yellow solid that turned brown on standing. The supernatant liquid was yellowish, and had no odor.

Salt.—Salt threw out a little monoethyl aniline, but the water layer retained a high color.

Precipitants.— $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$ were without effect on either color or odor.

Boiling.—Boiling did not improve odor in five minutes.

Filtchar.—Filtchar removed some odor, but even large quantities failed to remove very much.

Bleaching powder.—Bleaching powder in acid solution gave a dark purplish coloration. The character of the odor was changed and seemed phenolic. The color was not removed by Filtchar.

Dye.—Attempts to make an azo dye by adding the waste to diazotized arsol solution were fruitless.

Nitrous acid.—Nitrous acid caused the formation of a light colored precipitate that turned brown. The supernatant liquid was light yellow in color and had an odor that was somewhat improved, though phenolic in character.

Dilution.—A hundredfold dilution gave a liquid without odor or color.

Monoethyl Aniline Waste. Still Residue.

Bromine.—Bromine precipitated a brown solid, leaving a light yellow, odorless, supernatant liquid.

Filtchar.—Filtchar, above 1 per cent, removed all the odor and part of the color.

Bleaching powder.—Bleaching powder in acid solution caused a yellow colloidal solution to form, having no odor.

Ether.—Ether removed both color and odor.

Precipitants.— $\text{Fe}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$ all removed some color, but no odor.

Nitrous acid.—Nitrous acid caused a brown colloidal precipitate which could be carried down by $\text{Fe}(\text{OH})_2$, leaving a light colored, odorless solution.

Dilution.—Upon dilution 100 times, both odor and color were no longer perceptible.

Large scale experiments.—The experiments 1 and 2 under "Dye wastes" show the effect of monoethyl aniline waste upon the precipitation treatment of dye wastes. In experiment 1 (page 180) the dilution was about 21 times for the combined monoethyl aniline wastes, and it is seen that the effluent had a little odor.

In experiment 2 the final dilution was 84 times, and the odor was practically all gone.

Lagoon Liquor.

Precipitants.—When lagoon liquor was made faintly alkaline with lime a slight flocculent precipitation was noted, which consisted of the hydroxides of iron and zinc. These precipitants failed to carry down any of the color. Other precipitants, including PbSO_4 , $\text{Al}(\text{OH})_3$ also failed to carry down any color.

It was found, however, that a large amount of ferrous iron would carry down color when precipitated. A 200 cc. sample of lagoon liquor was treated with ferrous sulphate containing 0.017 grams of iron, and made alkaline. The filtrate effluent from this sample had most of the color removed. On standing 24 hours, however, the solution took on a purplish color. It is believed that the effect of the iron was more one of reduction than one of carrying down color. The purplish tinge was so faint that it disappeared nearly altogether when the liquor was diluted to six times its volume.

The iron present in the lagoon liquor was found to be in the ferrous state when tested with ferricyanide, ferrocyanide, and thiocyanate.

Distillation.—When lagoon liquor was distilled, the first 20 per cent distillate was found to have a strong earthy odor, but very little color. The remaining distillate had neither color nor odor.

Oxidation.—Lagoon liquor decolorized permanganate without itself being decolorized. Boiling lagoon liquor with strong nitric acid and then making it alkaline seemed to remove some of the color.

Bromine.—Bromine caused the precipitation of a fine solid, and practically the decolorization of the solution.

Bleaching powder.—Bleaching powder in acid solution had practically the same effect. Table II shows the effect of varying amounts of chlorine on the color, and the effect of various conditions of chlorination.

TABLE II.—*Effect of bleaching powder on lagoon liquor.*

Sample.	Grams of chlorine per liter.	Series C, alkaline lagoon liquor filtered. Color removal, alkaline.	Series D, acidified series C liquor. Color removal, acid.	Series E, lagoon liquor as found. Color removal.
1.....	0.4	Darker.....	None.....	Darker.
2.....	.8	do.....	do.....	Do.
3.....	1.2	do.....	do.....	None.
4.....	1.8	do.....	do.....	75 per cent.
5.....	3.0	70 per cent.....	do.....	90 per cent.

The 90 per cent color removal appears to be satisfactory, and it is seen that this requires 3 grams of chlorine per liter.

Absorbents.—In the laboratory it was found that charcoal, clay, blast furnace slag, open hearth slag failed to remove color from lagoon liquor.

Bone black, the Filtchar series, and Kelcar,¹ were all found to be effective in removing color. In testing the efficacy of these compounds they were simply stirred up in measured proportions with the lagoon liquor, and allowed to stand overnight. The solutions were then filtered, and the color removal was determined by testing against the Bismarck brown standard (see footnote to Table I). The set of curves (Fig. 3) shows the efficacy of the various absorbents used.

From these curves it is seen that in order to obtain an effluent having an absolute color of 10 p. p. m. Bismarck brown, the require-

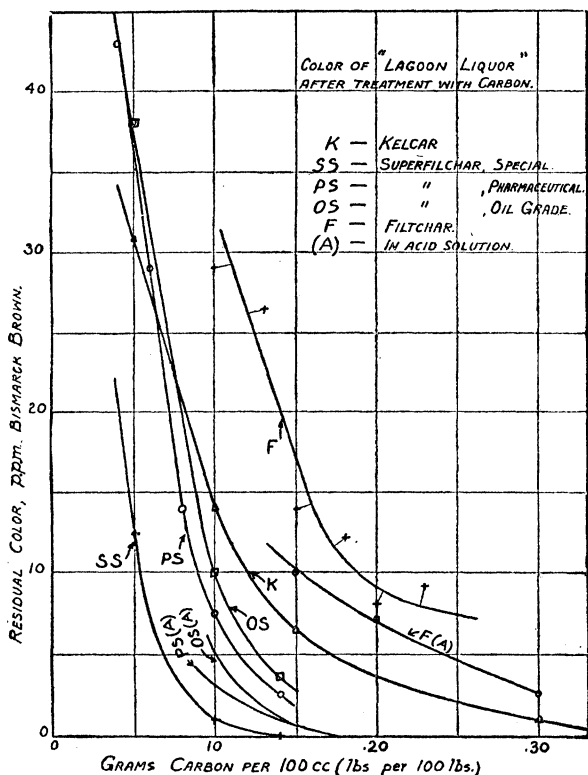


FIGURE 3.

ment was about 0.9 or 1.0 gram per liter of either Superfiltchar, about 1.2 gram per liter of Kelcar, and about 2.3 grams per liter of Filtchar. (The special Superfiltchar is not on the market.)

It is also seen that the color removal was better in acid than in alkaline solution. When these acid-treated solutions were made alkaline the colors were about the same as if they had been treated alkaline in the first place.

¹ Produced from Pacific coast kelp by R. B. Stringfield, Los Angeles, Calif.

Attempts were made to rejuvenate the Filtchar and Superfiltchar which had been used up in treating lagoon liquor. The result of these attempts was to develop a process by which the material was heated to about 1,300° F. in air for a short time, and allowed to cool in the absence of air. If air was not excluded during the cooling, the material smouldered at low red heat and never became cooled off.

A continuous process for treating exhausted Filtchar was contemplated, by which it was slowly passed through a trough con-

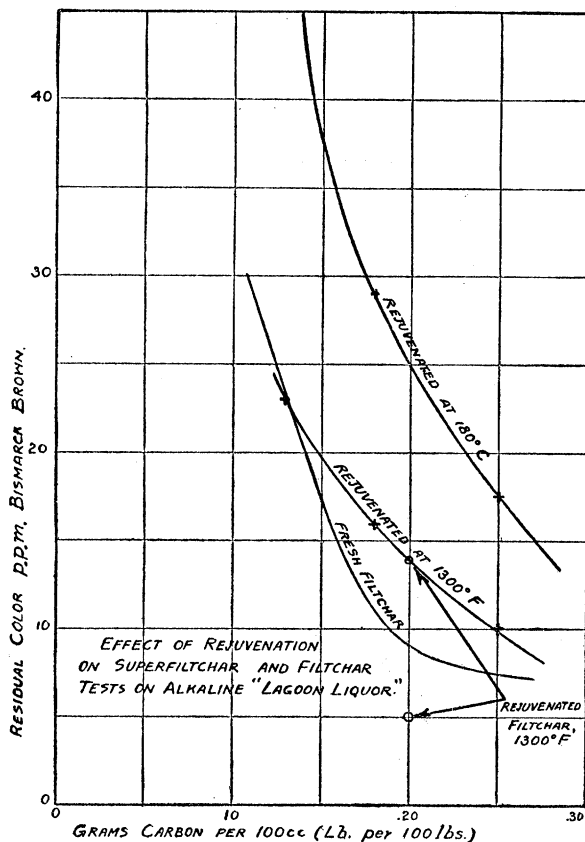


FIGURE 4.

veyor of the helical type, heated to the desired temperature. A small model of such a conveyor was operated and found to give good results. It was seen to be necessary, however, to break up all lumps, and to grind large particles fine, before passing through the heating chamber. The loss caused by conducting this heating in one stage in the laboratory averaged only 10 per cent. The set of curves (Fig. 4) shows the efficacy of rejuvenated Filtchar and Superfiltchar as compared with Filtchar as bought on the market.

From these graphs it is seen that the rejuvenated material is approximately in the same class as the fresh Filtchar.

One impractical feature of the continuous process is that the amount of fine dust caused is very great, and may perhaps entail large losses.

Large scale experiments.—In the 300-gallon treating plant, the best laboratory results of the chlorination and the Filtchar treating processes were tried out.

Experiment 1: Used 42.8 cubic feet of lagoon liquor; added 1.4 pound of bleaching powder (30 per cent chlorine, equivalent to 67.2 ounces chlorine); added 600 cc. of oleum.

The result of this treatment was a light brown sludge and a very light yellow, very slightly acid, supernatant liquid which had a slight odor of chlorine. It was considered a satisfactory effluent for discharge into the river.

Experiment 2 : 29.4 cubic feet of lagoon liquor was treated with 500 cc. of slaked lime; at this point the solution was alkaline to litmus.

To 25.5 cubic feet of supernatant liquid from this treatment were added 23 ounces of Superfiltchar (oil grade) and this was allowed to stand overnight (corresponds to 0.090 per cent Superfiltchar). When the resulting suspension was filtered the effluent had a yellow color of 38 p. p. m. Bismarek brown, but little odor or taste. From the color point of view it was unsatisfactory to discharge into the river.

Experiment 3: Same as experiment 2, except that 50 ounces of Superfiltchar were used with 35 cubic feet of alkaline lagoon liquor (0.142 per cent Superfiltchar).

The result of filtering this treated waste was an effluent having only 4 p. p. m. color, no odor, and only a taste of lime. It was considered a satisfactory product to discharge.

Experiment 4: Used 40 cubic feet of lagoon liquor and 100 cc. of slaked lime. Upon settling, the supernatant liquid was neutral to litmus, alkaline to methyl orange, and acid to phenolphthalein.

To 25.7 cubic feet of this supernatant liquid were added 68 ounces of ordinary Filtchar (0.260 per cent), and the mixture stood overnight.

The effluent from filtering this mixture had a color of 8 p. p. m., practically no odor and practically no taste.

Dye Wastes: Lake-forming Dyes.

The color in the wastes from the particular dyes, "guinea green" and "formyl violet," were found to be carried down by the precipitants, ferrous hydroxide and aluminum hydroxide. The results were much better when lime instead of soda ash was used as the precipitating agent.

Quantitative experiments showed that a slight excess of lime was necessary in order that the iron should give the best results. The color of the resulting supernatant liquor depended upon the amount of iron used, but could be almost entirely removed with enough iron. Any residual color was not much affected by the use of Filtchar. The effect of dilution was to weaken the carrying down power of the same amount of iron.

Experiments were performed on a mixture of wastes in the proportion in which they were expected to be discharged from the plant, including wash water, as well as some monoethyl aniline waste, which was a relatively uncolored waste. This proportion was as follows:

	Per cent.
Lake-forming wastes.....	45.1
Monoethyl aniline waste.....	4.9
Wash water.....	50.0
	<hr/> 100.0

With this mixture it was found that the actual coloring matter could be carried down by 0.4 pound of iron as FeSO_4 per thousand pounds of waste. But this left a rather intensely colored yellowish solution. By using 1.2 pound of iron per thousand pounds of waste over 99.5 per cent of all the color could be removed. This also required 9.6 pounds of lime as milk of lime per thousand pounds. The result seemed to be partially due to the reducing action of the ferrous sulphate, because some yellow color returned slowly upon oxidation in the air. The best results were inhibited by mixture of any nonlake-forming dye waste with this, because a brownish coloring matter was formed, which could not be removed with Filtchar.

The odor of the waste when treated with copperas and lime was not very pleasant, as there were faint traces of benzaldehyde, monoethyl aniline, and other odors in it. This odor was not much improved upon treatment with Filtchar, but disappeared on dilution of the waste with water. Partial evaporation of 40 per cent of the treated waste failed to improve the odor to any extent.

The taste was very salty from the salt used in the manufacturing process. Table III shows the effect of dilution upon the odor, taste, and color of the treated waste.

TABLE III.—*Effect of dilution upon the odor, taste, and color of the treated waste.*

Dilution.	Odor.	Taste.	Color.
Straight treated waste.....	Bad.....	Bad.....	18
One-fourth.....	Much improved.....	do.....	4.5
One-eighth.....	Very faint.....	do.....	2.3
One-eighteenth.....	None.....	Very salty.....	1
One-fortieth.....	do.....	Faint.....	0
One sixty-seventh.....	do.....	Very faint.....	0
One one-hundredth.....	do.....	None.....	0
One two-hundredth.....	do.....	do.....	0
One four-hundredth.....	do.....	do.....	0

From this table it is observed that a dilution of one-fourth gives an effluent satisfactory from the color standpoint, a dilution between one-fourth and one-eighth from the odor standpoint, and about one one-hundredth from the taste standpoint.

Azo-phloxine waste could be decolorized by copperas and lime. It appeared that a large quantity of each chemical was required to give the necessary decolorization.

Evaporation.—Evaporation experiments were performed to determine whether the salt contained in the wastes could be used again. Some of the salt obtained from both the guinea green and the formyl violet was used again for salting out guinea green and formyl violet dyes, respectively. The dyes thus precipitated were tested in the local dye laboratory and found to be as clean and as good as the dye salted out by fresh salt.

Bleaching powder.—Azo-phloxine waste could be largely decolorized with bleaching powder and acid. The resulting liquid was brownish in color and quite odorous from the chlorine and chlorinated products.

Large-scale experiments.—Experiment 1: A mixture of wastes, to simulate working proportions, was made as follows:

	Cubic feet.
Formyl violet.....	6.5
Guinea green.....	10.8
Monoethyl aniline still residue.....	.70
Monoethyl aniline receiver waste.....	1.20
Water.....	20.8
Total.....	40.0

To this were added solutions of ferrous sulphate containing about 15 ounces of iron and a half bucket of moist slaked lime weighing about 15 pounds. After agitating, this was allowed to stand overnight.

The supernatant liquid was of a quite intense yellow color and had a moderate odor. The color removal was 80 per cent.

A quantity of 14.2 cubic feet was treated in another tank with 30 ounces of Superfiltchar and 11 ounces of rejuvenated Filtchar.

At the end of two days the odor removal was nearly complete and the color removal was still about 80 per cent. In other words, the Filtchar removed odor but not color.

Experiment 2: Wastes were mixed together as follows:

	Cubic feet.
Guinea green.....	4.8
Formyl violet.....	2.9
Monoethyl aniline still residue.....	.31
Monoethyl aniline receiver liquor.....	.50
Water.....	8.6
Total.....	17.1

Added ferrous sulphate containing 30 ounces of iron (1.75 ounces per cubic foot, equivalent to 1.75 pounds per thousand pounds); added, with agitation, 20 pounds of moist slaked lime (9.4 ounces per cubic foot, equivalent to 9.4 pounds per thousand pounds).

Samples taken of the supernatant liquid after standing overnight showed a color removal of 99.5 per cent, absolute color of 18 p. p. m., and a rather limy odor which, on standing, gave way to a faint one of organic compounds. The volume of the sludge was about 70 per cent of the total volume.

This waste was agitated and filtered through the sand filters. It was found that with a 3-inch covering of iron sludge and a head of about 5 inches, the rate was about 34 gallons per square yard per hour.

The effluent from the sand filter was greenish in color, but it was seen that this color was caused by suspended iron hydroxide. On oxidation by air and filtering in the laboratory, the suspension was all removed; but the filtrate was brown in color—about 80 p. p. m. Bismarck brown. On diluting this six times, the laboratory sample was seen to have a satisfactory color and practically no odor.

Nonlake-Forming Dyes.

Precipitants.—The nonlake-forming dye wastes were those from the manufacture of the “direct green” series of dyes. It was found that the following precipitants failed to carry down any color: $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$.

When the waste was mixed with the lake-forming wastes and given the precipitation treatment, it was found that the effluent was of dark green color instead of a light yellow. This color was not removed by treatment with 1.5 per cent Filtchar.

If the waste was acidified and filtered before addition to the lake-forming wastes, and then given the precipitation treatment, the color of the filtrate was dark brown, and could be reduced to 15 p. p. m. Bismarck brown by treatment with 3 per cent Filtchar or 3 per cent Kelcar.

Acid.—Sulphuric acid caused a considerable foaming, but no color change. The liquid was then filtered and a dark slimy substance was removed. Upon treatment of this filtrate with Kelcar or Filtchar, there was little improvement in color. If, instead, it was treated with copperas and lime, and then with Filtchar, there was still little color improvement.

Reduction.—The reducing effect of ferrous sulphate was practically nil. By vigorous reduction with hydrogen from zinc and acid, most of the color was removed. Part of this returned on oxidation by the air.

III. RESULTS.

The results of this investigation show by what methods the various wastes produced in the manufacture of some dyes and intermediates can be treated. These treatments include chlorination, precipitation, and absorption.

The treatment for each waste or group of wastes will depend upon the relative cost, it being desired, of course, to achieve the best results at the lowest cost. The estimated relative costs of the various processes are given below. These include only those costs of each process that are not common to all the processes. For example, such a common cost would be the making alkaline of an acid waste.

TOLUIDINE WASTE.

TABLE IV.—*Comparative costs of treating Toluidine waste.*

Method.	Color of treated waste, p. p. m. Bismarek brown.	Odor of treated waste.	Cost per pound of waste.	Cost per 1,000 gallons.	Cost per pound of product.
Chlorination, 30 grams of chlorine to the liter (at \$0.06).	Medium brown...	Rather strong...	\$0.0018	\$15.00	\$0.0060
Evaporation.....0006	5.00	.0020
Bone black, 0.9 pound to the cubic foot (\$0.09 per pound).	About 5.....	None.....	.0013	10.80	.0043
Filtchar, 8 pounds per 1,000 (\$0.06 per pound).do.....do.....	.00048	4.00	.0016
Superfiltchar, 3 pounds per 1,000 (\$0.14 per pound).do.....	Faint.....	.00042	3.50	.0014

The cost of the Filtchar and Superfiltchar treatments is seen to be slightly under the cost of evaporation, while all others are higher. The advantages of the Filtchar treatment over evaporation are that it requires less equipment, and is more flexible as regards the quality of the treated waste. Furthermore, there is a possibility that exhausted Filtchar can be cheaply rejuvenated. The advantage of the Filtchar treatment over the Superfiltchar treatment is that the Filtchar is likely to be a stable product on the market, whereas the Superfiltchar is more of a special product.

LAGOON LIQUOR.

The cost of treating the lagoon liquor should be cut down as low as possible because it is of such a large volume and represents no income from production. The rejuvenation of exhausted Filtchar offers the best possibilities. If it is to be considered that the loss by rejuvenation is 10 per cent each time, we can determine the life of 1 pound of Filtchar by summing the decreasing geometrical series, $1 + (0.9 \times 1) + [0.9 \times (0.9 \times 1)] + \dots$, which converges to a definite limit. The sum of this series is 10. In other words, by rejuvenation,

1 pound of Filtchar becomes the equal of 10 pounds of fresh Filtchar, theoretically. If Filtchar is \$.06 per pound, the equivalent in rejuvenated Filtchar is \$.006 per pound. Adding \$.01 per pound to this for the cost of rejuvenation we arrive at a total estimate of \$.016 per pound for material.

TABLE V.—*Comparative costs of treating lagoon liquor.*

Method.	Color of treated waste, p. p. m. Bismarek brown.	Odor of treated waste.	Cost per pound of waste.	Cost per 1,000 gallons.
Evaporation.....			\$.0006	\$5.50
Chlorination: 3 grams of chlorine to the liter (at \$.06 per pound).....	12	Very slight....	.00018	1.00
Superfiltchar: 0.85 gram to the liter (pharmaceutical, at \$.19 per pound).....	12do.....	.00016	1.33
Superfiltchar: 0.95 gram to the liter (oil grade at \$.14 per pound).....	12do.....	.00013	1.08
Filtchar: 1.7 grams to the liter (\$.06 per pound).....	12do.....	.00010	.83
Filtchar: 2.5 grams to the liter (\$.06 per pound).....	8do.....	.00015	1.25
Rejuvenated Filtchar: 2.5 grams to the liter (\$.016 per pound).....	8do.....	.00004	.332
Kelcar: 1.1 grams to the liter (\$.045 per pound).....	12do.....	.000050	.41
Precipitation and dilution: Lime, at \$.008 per pound, 9.6 pounds to 1,000 pounds of waste; FeSO_4 at \$.010 per pound Fe 1.2 pounds to 1,000 pounds of waste	15do.....	{ .000077 .000012 .000089 }	{ .74

Table V indicates that the treatment of the waste by Filtchar in connection with a process for rejuvenation for the latter offers the best prospects for treatment at low cost. The treatment by precipitation and dilution is nearly as cheap in material, and is likely to be much more convenient in practice as there will not be the rejuvenation process to be handled. Furthermore, the precipitation process has the advantage of being a duplicate of the process recommended for the lake-forming dye wastes.

The treatment by Kelcar without rejuvenation is also a very cheap process, and its only disadvantages are the uncertainty of the supply and the distance it must be shipped (Los Angeles, Calif., to Springfield, N. J.).

LAKE-FORMING DYE WASTES.

The most effective treatment for lake-forming dye wastes was found to be the precipitation treatment followed by dilution.

TABLE VI.—*Comparative costs of evaporation and precipitation methods of treating lake-forming dye wastes.*

Method.	Residual color, p. p. m. Bismarek brown.	Cost per pound of waste.	Cost per 1,000 gallons.
Evaporation.....		\$.0006	\$5.00
Precipitation.....	15	.000089	.74

Table VI does not give a true comparison of the costs of the two methods enumerated, because salt having value would be obtained as a product of an evaporation. To carry out such a method of

evaporation it would be necessary to separate each actual waste liquor from the wash water of the tanks, filter presses, etc., and evaporate only the former, each waste separately. The wash water, on account of very low concentration of coloring matter, could be quite cheaply treated with copperas and lime.

IV. SUMMARY.

Investigations have been carried out as to properties and disposal treatment of several wastes of the dye and intermediate industries. Laboratory studies were made of the properties of toluidine waste, nitrobenzene waste, monoethyl aniline waste, dye wastes, and lagoon liquor.

Treatments that were successful on a 300-gallon scale and that were cheaper than evaporation were found for the lagoon liquor, the monoethyl aniline wastes, and the lake-forming dye wastes; and a method of treating toluidine waste was indicated in laboratory experiments.

Specific treatments of wastes were recommended ¹ to the Chemical Company of America, based on their proposed production schedule. For the lake-forming dye wastes and monoethyl aniline wastes this treatment was as follows:

1. A mixture together of all the wastes and wash waters except the waste and wash water from the manufacture of the "Direct green" series of dyes.

2. Addition and dissolving of ferrous salt in the proportion of 1.2 pounds of iron per thousand pounds of solution. This can be done in a wooden vat.

3. Addition, with agitation, of slaked lime in the proportion of 8 pounds of $\text{Ca}(\text{OH})_2$ per pound of Fe (or 9.6 pounds of $\text{Ca}(\text{OH})_2$ per thousand pounds of solution). This amount is in addition to the amount necessary to neutralize the acid in the waste if any should occur.

4. Filtration with or without settling of the supernatant liquid. This can be done by means of a sand filter bed or any other suitable filtering medium.

5. Dilution of the effluent from the filter with five times its volume of water.

6. Daily removal of the solid sludge from the filter to suitable dumps or hollows.

7. The only cheap method found for disposal of the "Direct green" dye wastes is evaporation.

APPENDIX.

There is given below a systematic set of steps for experimental treatment of wastes. Realizing that evaporation is the simplest form of treatment for liquid effluents, the figures given below are

¹ The plant recommended has been constructed and is operating with entire satisfaction.

the maximum quantities of materials that can be used in order that the process be cheaper than evaporation. They are based on market prices in June, 1919.

- (1) Try aeration for blowing out bad odors.
- (2) Try Filtchar up to 8 pounds per thousand of waste for removing odor and color.
- (3) Try chlorine (in both acid and alkaline solution) up to 8 pounds per thousand for improving odor and color.
- (4) Try copperas and lime for precipitating color; also alum and lime, etc.
- (5) Try boiling for removing bad odors.
- (6) Try partial evaporation for removing bad odors.
- (7) Try strong reducing agents; also strong oxidizing agents.
- (8) Try strong alkali up to 5 pounds per thousand of waste.
- (9) Investigate the manufacturing process with reference to making use of the waste again several times. For instance, in the case of the residue from the manufacture of toluidine by acid reduction of nitrotoluene, this waste might be fortified with strong acid and used again.
- (10) Try shaking out with ether up to 5 pounds per thousand of waste.
- (11) Try dilution.
- (12) Try bacterial action.

If no satisfactory improvement is obtained by any one or combination of these schemes, then the special chemical and physical properties of the objectionable constituents should be studied.

For instance, an aldehyde might be oxidized to an acid having an insoluble lime salt, or a nitro compound might be reduced to form an amine removable by Filtchar. An aromatic primary amine might be precipitated as an azo compound.

Other absorption compounds than Filtchar, such as Kelcar, Norite, coke, talc, fuller's earth, should be studied if they offer cheaper possibilities.

With special reference to dyes which are salted out, there is a good field for studying the recovery of salt from the wastes by evaporation.

It should be remembered in any case that the waste must be made alkaline after treatment if it is not already so, and should be allowed to stand in air as a test, for it will be oxidized as well as made alkaline in the river.

The removal of the dyes by electrical precipitation may be a field for study. It could not be studied at the experimental plant for lack of direct current power.